Indian J. Phys. **64A** (1), 1-9 (1990)

Effect of annealing and hydrogenation on the magneto-thermo-emf of nickel

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Received 5 August 1988, accepted 3 October 1989

Abstract : Changes in the thermo-emf due to externally applied magnetic field in a nickel wire pre-annealed at different temperatures have been measured both before and after hydrogen treatment i.e. cathodic hydrogen diffusion and subsequent outgassing. The hydrogen treated wires give a more regular ΔE ($\mu V/°C$) vs annealing temperature curve than those not subjected to hydrogenation. It is pointed out that after the hydrogen treatment wires contain hydrogen trapped at the lattice defects sites which make the lattice electrically more homogeneous.

Keywords : Annealing and low temperature aging, hydrogen diffusion, thermo magnetic effect.

PACS Nos : 72.15 He, 72.20 Nz, 73.50 Jt.

1. Introduction

The diffusion of hydrogen in metals is a subject of both basic as well as applied importance. A review of the various aspects is given by Alefeld and Völkl (1978). In our laboratory, various transport properties of cathodically hydrogenated nickel have been studied. A nickel wire on hydrogenation becomes brittle. If left to itself it loses hydrogen with time. During this period of outgassing the following properties were studied by us : thermoelectric variation with time (Nigam and Garg 1972, Nigam and Rani 1975 and Kapoor and Nigam 1987) resistivity changes (Nigam and Rani 1977, 1978), Hall coefficient changes (Rani and Nigam 1978) and thermal conductivity of nickel hydrogenated for different time (Kapoor and Nigam 1988). The sample of a nickel wire left after hydrogen outgassing will be referred to as the hydrogen treated sample. Further, the development of stress during hydrogenation of nickel was investigated by Misra and Nigam (1982). There are two common features in the results of all these different studies :

(a) The thermal history of the sample is very much effective in deciding the extent of hydrogenation of samples. Samples annealed at high and low temperatures show different behaviours. Even, the very low temperature-annealing creates certain changes which persist even after bringing the sample to the room temperature (Kapoor and Nigam 1987).

(b) During the outgassing all the physical properties tend to approach their original values but never attain them even if, one waits for several months. Thus the hydrogen-treatment creates some long-lived changes, that also depend on the pre-annealing temperature of the specimen.

The present paper reports the variation in the thermomagnetic effect due to annealing and hydrogen treatment of nickel. The justification for this study lies in the following facts :

(a) The effect of vacancies and defects on the electrical resistivity of conductors has been widely studied both theoretically as well as experimentally (Nigam and Rani 1982). Such investigations on thermo-emf have been reported only recently (Nigam and Gupta 1988). However, thermomagnetic effects have never studied from this point of view.

(b) The classical theory of the change in thermopower due to an external magnetic field as discussed by Landau and Lifshitz (1982), has been based on thermodynamic considerations and predicts a linear dependence on applied magnetic field. The review of Jan (1957) classifies the above effect as a thermomagnetic effect and quotes Sondheimer formula derived on the basis of two band model (Sondheimer 1948). The expression is quadratic in B the field strength. The only quantity that connects the solid state characteristics with this effect is the resistivity. As such, it is difficult to predict from this expression, how annealing is going to alter the magneto-thermo-emf. The only possibility at present, is to carry out an experimental investigation.

(c) Gupta and Nigam (1984a, b) showed that whereas cold work creates dislocations in the annealed nickel wire samples, the hydrogen diffusion tends to restore the original state. It was shown by Lee and Lee (1986a, b) that hydrogen gets trapped at the vacant lattice sites. It is proposed in the present work that this trapping of hydrogen makes the defective lattice electrically and magnetically more homogeneous.

2. Experimental

Samples of nickel wires consisted of wires having 0.25 mm diam., 20 cm length. They were vacuum annealed at 210°C, 110°C, 0°C, −196°C and −269°C. The samples were then electro-polished. Cathodic hydrogen diffusion was done by the method of Baranowski and Smialowski (1959) i.e. Ni wire samples were made the cathode and a Pt wire the anode, while the electrolyte consisted of a solution of 10 cc of H_2SO_4 per litre of distilled water containing 0.2 gm of thiourea as an inhibitor. The electrolysis current was kept at 30 mA and was supplied by a 6 V lead accumulator. The duration of electrolysis was 200 hrs. Hydrogen evolved at the cathode diffuses slowly in the nickel wire sample. Such samples of nickel wire become brittle on hydrogen saturation and were used in our earlier studies when it was intended to follow the changes in physical properties during hydrogen outgassing. Complete outgassing takes 7-8 hours of time. Even after this time-period the physical properties do not attain their original value. Thus, we have two sets of annealed samples :

(a) One set consisted of annealed samples not subjected to hydrogen treatment.

(b) Another set is of annealed samples all subjected to the above mentioned hydrogen treatment.

The change in thermo-emf of the above samples in an external magnetic field was studied as follows. Thermocouples of nickel wire were made with copper wire, the latter being a non-ferromagnetic substance, shows a change in thermo-emf due to a magnetic field only by about 10^{-7} volts/°C whereas ferromagnetic nickel by $\sim 10^{-6}$ volts/°C. The cold jucntion was dipped in a cup of mercury cooled by melting ice while the hot one was kept in mercury maintained at room temperature. The temperatures of both the junctions were measured continuously during the entire observation period with the help of thermometers dipped in mercury. Sommerfeld and Frank (1931) have criticised the bending of wires in the region of the magnetic field as was done earlier. To keep both the junctions in the same field is practically difficult. Konsmine (1934) while performing experiments with ferromagnetic materials, has stressed that the external field can be applied anywhere in the sample since it ultimately magnetises the whole length of the ferromagnetic wire. He has performed experiments both with longitudinal as well as with the transverse fields. In former, it matters little whether the whole wire is in the magnetic field or not. The curve for change in thermopower with applied field are very nearly the same. In case of transverse field, if the whole sample is inside the field, a lower value of field can produce the same change in the thermopower as a higher value for a sample kept in whole in the field. The curves for the variation in thermopower change with B have similar shapes but are displaced with respect to each other along the x-axis réperesenting the B-values. In case of wires, it is not possible to put the whole sample in field. Further in Konsmine' experiments the junctions were not in region of uniform field produced by the Helmholtz coils. In the present studies, the hot junction was kept in the magnetic field. For this reason the hot junction consisted of a glass tube (5 mm diam) containing mereury at the bottom into which the junction was dipped. This was kept between the pole pieces of a strong electromagnet as shown in Figure 1. The magnetic field applied, was in the range of 8.6 to 22 kilogauss. The two ends of the thermocouple were connected to a D.C. amplifier with gain 100 supplied by M/s Sensing Devices, Kanpur and the output was read by a digital voltmeter. First the thermo-emf with zero field was measured. Next the magnetic field was slowly applied and the steady reading in the millivoltmeter was taken. After each

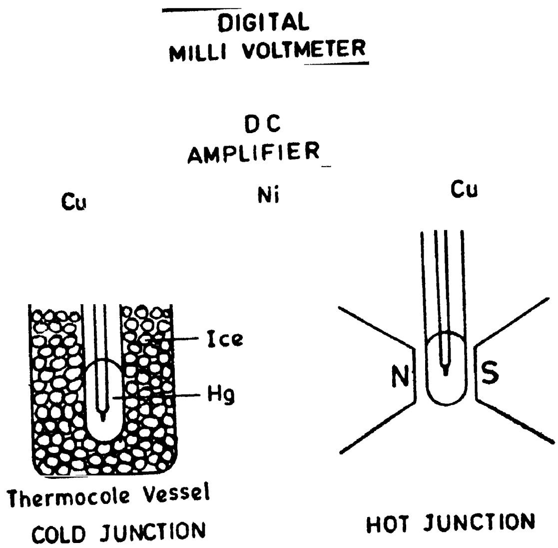

Figure 1. Schematic arrangement for measuring change in thermo-emf under applied magnetic field.

increase in the magnetic field the millivoltmeter showed some fluctuations but gave a steady reading after a few minutes. Again we stress that copper shows a minor (negligible) change in thermo-emf compared to nickel and therefore, the observed changes were attributed to nickel alone.

3. Results and discussion

Table 1 collects data on the thermo-emf variation with applied magnetic field for various samples both before and after hydrogen treatment. Copper thermopower ($+3.3\ \mu V/^{\circ}C$) has not been subtracted out. The data was taken during increasing magnetic field to avoid hysteresis that occurs in the decreasing sequence of the field. Figure 2 shows a plot of this variation of thermo-emf with the field strength for differently annealed samples. Konsmine (1934) found a saturation at 1500 Gauss for pure nickel. In our case, this does not persist even at higher fields. Further this figure shows that samples annealed at low temperatures behave in different manner than those annealed at higher ones. Different annealings cause different kinds of relative orientations of the crystal planes at the surface as revealed by measurement of their electrode potentials (Gupta and Nigam 1984a, b).

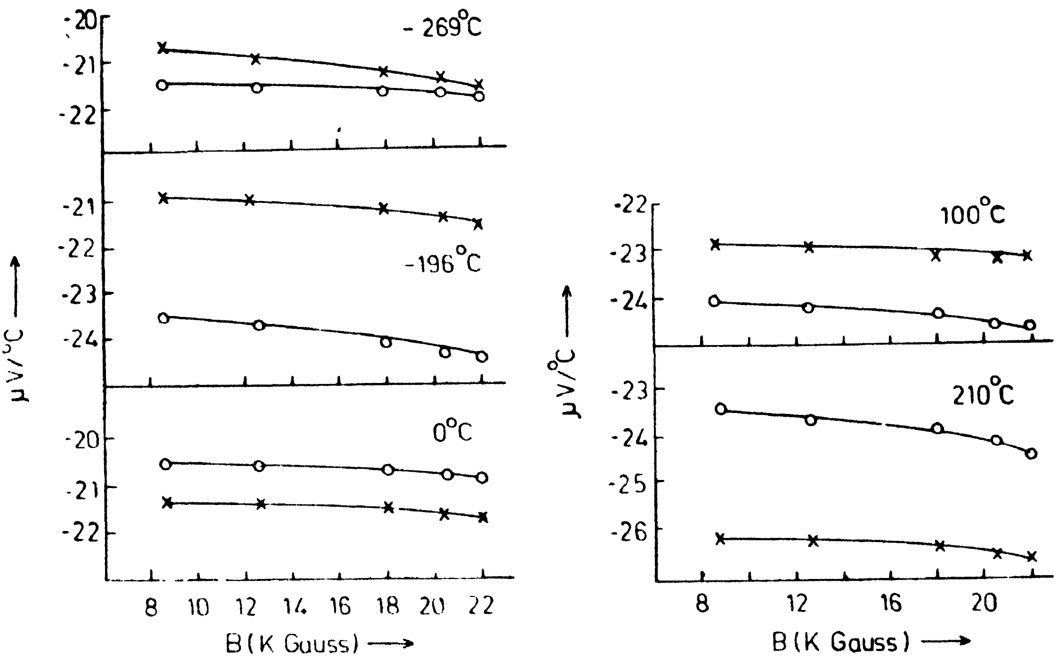

Figure 2. Variation of thermo-emf with applied magnetic field.

A better regularity is seen in Figure 3 (a, b) where, the change in thermo-emf due to different magnetic fields is plotted against the pre-annealing temperatures.

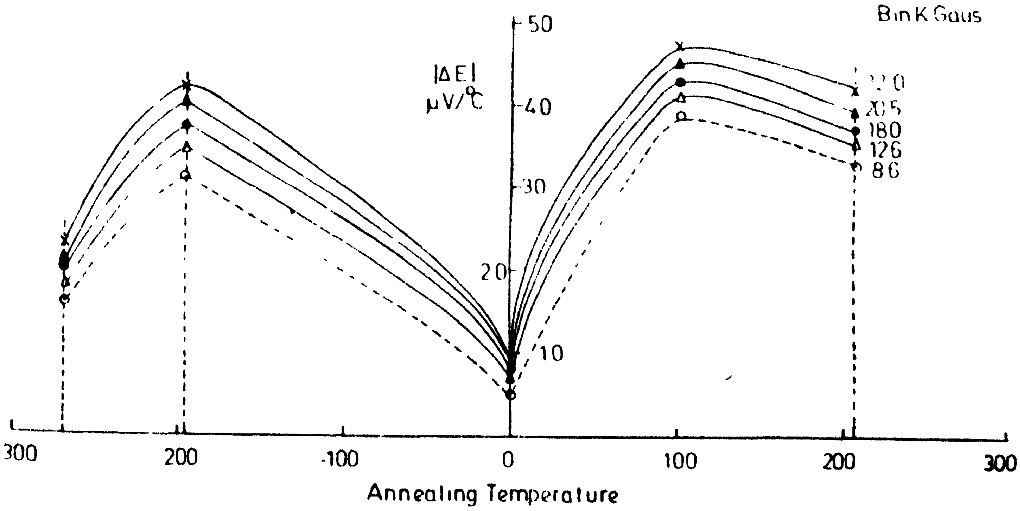

Figure 3(a). Variation in $|\Delta E|$ with annealing temperature before hydrogen diffusion.

As is evident, these changes are beyond the experimental errors. Both Figures 3 (a and b) show an interesting set of curves. Before hydrogen treatment, the low temperature annealed samples behave differently from the corresponding ones after hydrogen treatment. Figure 3(a) shows a symmetrical set of curves about 0°C annealing temperatures but Figure 3(b) shows distinctly a different kind of regularity.

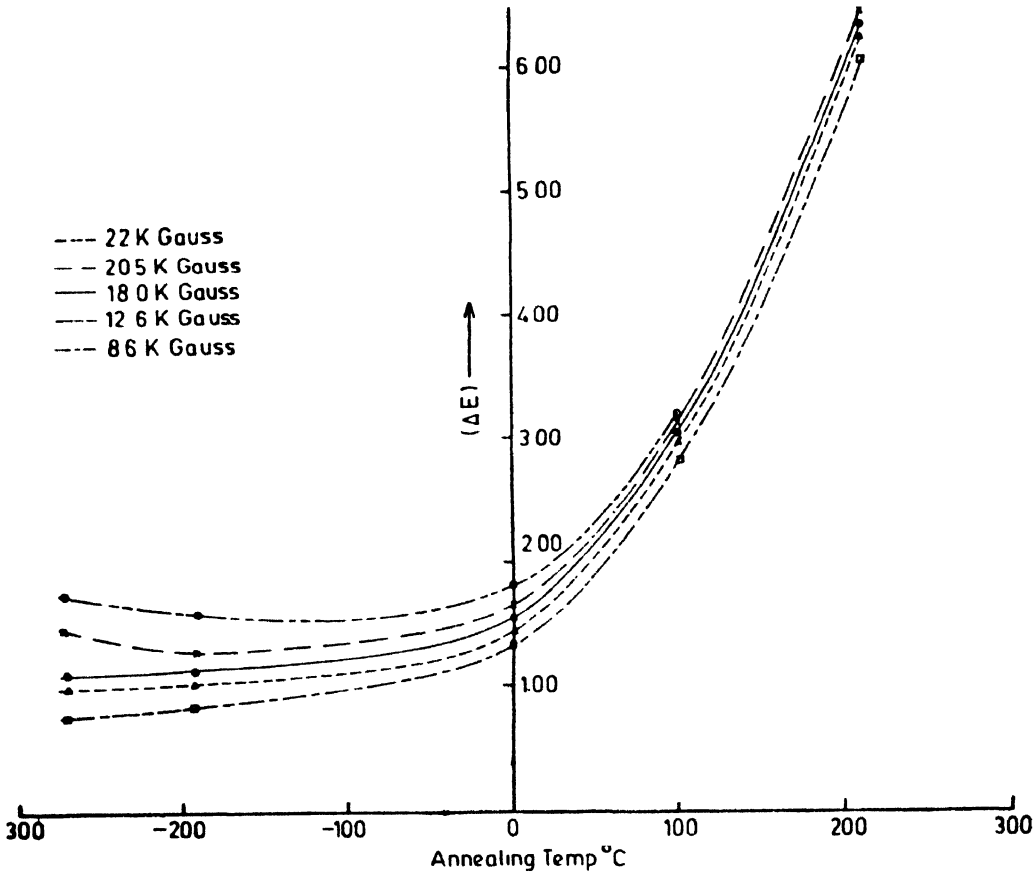

Figure 3(b). Variation in $|\Delta E|$ with annealing temperature after hydrogen diffusion.

When hydrogen is diffused in a metal, it gets divided into two categories : (a) the mobile part which is outgassed on its own if the hydrogenated metal is left to itself, (b) the trapped part which does not leave the metal unless special efforts to remove it, are made. In his review article Wert (1978) describes four kinds of trappings of pressure-diffused hydrogen in a metal : (i) Accumulation of hydrogen in voids produced by coalescence of vacancies. Solubility of hydrogen at lower temperature shows deviation from Arrhenius law. The site of lowest energy is an interstitial site near the vacancy but away from the centre. (ii) Accumulation of hydrogen in regions of high strain fields. The elastic and compressive stresses below the elastic limit appreciably modify hydrogen solubility. In such cases, introduction of hydrogen by pressure diffusion does not create or destroy the defects. (iii) Trapping by grain boundaries occurs but such sites are too few. This process is dominated by (ii) mentioned above.

Table 1. Variation of thermo-emf with magnetic field.

Annealing temperatures in °C	Applied magnetic field in K. Gauss	Thermo-emf in micro volts/°C			
		Pure metal		After hydrogenation and subsequent outgassing	
		Total E	ΔE	Total E	ΔE
210	0.0	20.06	0.0	20.06	0.0
	8.6	23.36	3.3	26.14	6.08
	12.6	23.59	3.53	26 23	6.17
	18.0	23.82	3.76	26.36	6.30
	20.5	24.05	3.99	26.50	6.44
	22.0	24.36	4.30		
100	0.0	20.06	0.0	20.06	0.0
	8.6	24.04	3.98	22.87	2.81
	12.6	24.22	4.16	22.95	2.89
	18.0	24.40	4.34	23.04	2.98
	20.5	24.61	4.55	23.08	3.02
	22.0	24.80	4.74	23.13	3 07
0	0.0	20.06	0.0	20.06	0.0
	8.6	20.54	0.48	21.38	1.32
	12.6	20.63	0 57	21.46	1.40
	18 0	20.67	0.61	21.58	1.52
	20.5	20.83	0.77	21.71	1.65
	22 0	20.91	0.85	21.83	1.77
−196	0.0	20.06	0.0	20.06	0.0
	8.6	23.50	3.14	20.91	0.85
	12.6	23.50	3.50	21.09	1.03
	18.0	23.80	3.74	21.13	1.07
	20.5	24.10	4.04	21.35	1.29
	22.0	24.30	4 24	21.61	1.55
−267	0.0	20.06	0.0	20.06	0.0
	8.6	21.61	1.55	20.82	0.76
	12.6	21.69	1.63	21.05	0.99
	18.0	21.74	1.68	21.32	1.26
	20.5	21.78	1.72	21.64	1.58
	22.0	21.87	1.81	21.86	1.80

Solubility in polycrystalline Ni is linear at high temperatures but is enhanced at low temperatures. (iv) Dislocation trapping studies are confined mainly to iron but accelerated hydrogen evolution from iron and nickel has been observed during plastic flow.

During cathodic hydrogen diffusion, there is a development of stress in nickel (Misra and Nigam 1982) but to say that there is no creation of new defects is not admissible according to Lee and Lee (1986a, b). Thus (ii) is ruled out for annealed nickel. Enhanced solubility of hydrogen diffused at low temperatures has been observed by us. The accumulation of hydrogen (H) at grain boundaries is not going to contribute to electrical and magnetic homogeneities. We, therefore, confine ourselves to the views (i) and (iv), where the vacant sites can trap H^+ ions which make the defect-lattice electrically more homogeneous.

Grain boundaries can trap H atom which will contribute to the paramagnetism of the metal but the hydrogenated nickel metal becomes again ferromagnetic after losing the hydrogen-contributed electrons from its conductions band (Bauer and Schmidtbauer 1961). Thus the grain boundary trapped hydrogen atoms make a small contribution to the magnetic properties.

From Table 1, it is clear that for the low temperature aged samples it is not the thermo-emf of Ni but the magneto-thermo-emf which is affected by hydrogenation.

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